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Interim report on the comparison of antisolvent crystallization vs. EFC for producing battery-grade MSA salts

This report is an interim report comparing two techniques for crystallizing battery-grade methanesulfonic acid (MSA) salts of the cathode metals Ni, Co and Mn withing the scope of a hydrometallurgical process for battery recycling. Technique 1 is crystallization driven by the addition of an organic solvent to the aqueous MSA solutions containing the metals, whereby the solubility is reduced leading to supersaturation of solid phases (‘antisolvent crystallization; ASC’). Technique 2 is crystallization by means of reducing the temperature until a eutectic point allowing metal salts and ice to be recovered simultaneously, driven by the removal of heat (‘eutectic freeze crystallization; EFC’).

General considerations for comparison of the two techniques

In general, EFC has several benefits for crystallizing metal salts from aqueous solutions. At the eutectic point, the yield can be controlled through the application of cooling, resulting in simultaneous crystallization of water to ice and metal salts at approximately constant conditions. For a pure system the theoretical yield is 100% at constant temperature conditions. The presence of impurities, other components or excess acid will complicate the situation; see below. Moreover, since water ice has lower density than the solution while metal salt solids have higher density, free ice crystals will float while the salt crystals will be recoverable from the bottom of the equipment.

The main drawbacks of EFC are related to ice scaling and energy. The highest local supersaturation as well as local free energy reduction is generated on equipment surfaces. Thus, ice crystals will tend to form and grow on the walls of the tank, on heat transfer areas, moving parts, etc. This scaling or incrustation can lead to at least three problems: i) problems recovering or cleaning the equipment, ii) loss of yield because ice crystals could encapsulate or include metals, and iii) a gradual loss of heat transfer efficiency. Practical solutions for reducing scaling may include scrapers and surface modifications of equipment; both of which entail material costs as well as increased running costs. Another potential issue with EFC is related to the thermodynamics. The feasibility of the technique for each specific system depends on the practical accessibility of the eutectic conditions. If the eutectic temperature is too low, costs of equipment and cooling can become prohibitive. Overall, EFC is not a very mature technology, and the level of know-how and the availability of specialized equipment are both low.

With respect to antisolvent crystallization, this is a more mature technology in an overall sense, being long in use in other fields, including the pharmaceutical industry, although it is not as yet a well-established technique for industrial-scale applications in hydrometallurgy. The main benefits of ASC include its comparative simplicity as a process, and its (theoretical) tuneability in terms of controlling product properties, selectivity and yield based on process variables as well as the availability of a wide range of potential antisolvents. Good scalability and potential for high yield are other advantages with ASC in general. The possibility to work at low temperatures is an advantage compared to EFC, as it does not entail the need for cooling equipment nor the energy consumption associated with it.

The main drawback of ASC compared to EFC is tied to the need to add another chemical to the system to drive supersaturation generation. The antisolvent is typically, although not necessarily, an organic solvent. For one, this introduces safety aspects into the process, as many organic solvents are hazardous, volatile and flammable. Secondly, the cost of the antisolvent necessary to produce a given amount of metal salts needs to be accounted for in the overall economic analysis. The cost and sustainability aspects of an ASC process can be mitigated by a separation step such as distillation, which is often a suitable technique for separating volatile solvents from aqueous systems. Finally, as for EFC, the availability of the technique requires the necessary thermodynamic framework is determined and favourable for a process (data on solubilities as functions of antisolvent type and amount, as well as data on miscibility).

For both techniques, the presence of impurities or other components will complicate the ideal situation. Impurities can become incorporated into the salt crystals in different ways, depending on the process conditions as well as the chemistry:

- Incorporated into the crystal structural lattice
- Co-precipitating into separate particles of other solid phases
- Encapsulated as droplets inside the crystal material
- Adsorbed from the dried mother liquor onto crystal surfaces

For EFC, as for cooling crystallization, it is typically easier to control crystal growth to limit impurity incorporation in the salt crystals. Care should be taken to limit ice scale formation, and to select materials that limit agglomeration and incrustation. With proper knowledge of the thermodynamic phase diagram of the entire system, the possibility to sequentially obtain solid phases is facilitated. This may be laborious work to compile, although thermodynamic modelling software may be of help here.

For ASC, apart from proper selection of a system, controlled addition of the antisolvent in conjunction with controlled hydrodynamics are of paramount importance to reduce impurity problems. The antisolvent should be added close to high-shear regions near the impeller, at a controlled rate, to limit local supersaturation effects that lead to uncontrolled precipitation of solid phases. Such precipitation can include different solid phases co-precipitating, and typically result in poor product properties (low crystallinity, agglomerated particles and impurity incorporation problems). The hydrodynamics should be considered, to maximize homogenization while minimizing secondary nucleation and agglomeration.

Specific considerations for comparison of the two techniques for producing battery-grade MSA salts

ASC of MSA salts of Co, Ni and Mn from pure synthetic solutions containing each respective metal in aqueous solutions of MSA have been performed at lab scale as an initial step to evaluate the potential of the technique for recovery of battery-grade salts. A number of organic antisolvents have been evaluated at different organic to aqueous ratios and at different process conditions. In contrast to what has previously been observed for leachates of other acids, most cases did not result in precipitation at all within a reasonable time frame. In addition, several systems resulted in suspected or confirmed liquid-liquid phase separation; a situation not ideal for designing a controlled ASC process. Overall, the work shows that ASC can be feasible for recovery of MSA salts of all three transition metals. However, more work needs to be done to establish optimum conditions (solvent, compositions, temperature, etc.)

For EFC, a lab-scale setup consisting of insulated batch cooling crystallizer with an overhead stirrer, and a temperature logger, has been designed and tested. Overall, it is shown that the technique works for these systems. Eutectic conditions are not at inaccessibly low temperatures, and MSA-salt and ice crystals are produced and can be separated using the setup evaluated. EFC experiments are still at early stages, and more work is needed to evaluate optimum process conditions and compare the resulting yields and product properties.